

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 619 277 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
23.12.1998 Bulletin 1998/52

(51) Int. Cl.⁶: **C04B 24/32**, C08F 222/06
// (C08F222/06, 299:00,
216:14)

(21) Application number: 94302384.6

(22) Date of filing: 05.04.1994

(54) Cement dispersant composition for inhibition of slump-loss

Dispergiermittelzusammensetzung für Zement zur Inhibition von Flüssigkeitsverlust

Composition dispersante pour ciment inhibant la perte de fluidité

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IE IT LI LU MC NL
PT SE

(30) Priority: 05.04.1993 JP 78024/93

(43) Date of publication of application:
12.10.1994 Bulletin 1994/41

(73) Proprietors:
• W.R. GRACE & CO.-CONN.
New York New York 10036-7794 (US)
• NOF CORPORATION
Tokyo 100 (JP)

(72) Inventors:
• Honda, Susumu
Tokyo (JP)
• Hara, Tadas
Ichikawa-shi, Chiba-ken (JP)

• Koyata, Hideo
Izumik-ku, Yokohama-shi, Kanagawa-ken (JP)

(74) Representative:
Jones, Helen Marjorie Meredith et al
Gill Jennings & Every,
Broadgate House,
7 Eldon Street
London EC2M 7LH (GB)

(56) References cited:
EP-A- 0 373 621 FR-A- 2 668 773

• CHEMICAL ABSTRACTS, vol. 107, no. 2, 13 July
1987, Columbus, Ohio, US; abstract no. 11972x,
YASUMURA JIRO & AL 'Cement additives for
improving fluidity and workability of cement
mixtures' page 298 ;column R ; & JP-A-62 017
055 (IDEMITSU PETROCHEMICAL CO., LTD) 26
January 1987

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 619 277 B1

Description

BACKGROUND OF THE INVENTION

5 The present invention relates to a cement admixture composition. More particularly, it relates to an admixture composition for hydraulic cement compositions such as mortar and concrete to prevent time wise decrease in their flowability (herein called as "slump loss") while drastically improving the compositions workability and applicability over sustained periods of time.

Slump loss is a major problem in the concrete industry. It is highly desired to have a cement additive which will impart high degree of flowability over an extended period of time while not imparting any significant set retardation to the cement composition. Various proposals have been made to solve this problem but, such proposals have not provided a combination of the desired characteristics or only provide the desired characteristics in low degrees.

Slump-loss is the biggest problem in concrete industry, and various methods have been tried by many investigators to solve this problem, but satisfactory solution has not been found so far. Therefore, there is a strong desire to find an early solution to this problem.

It is generally known, for example, that the copolymers of alkenyl ethers and maleic anhydride and the derivatives thereof can be employed as cement additives to improve slump loss [Japanese Patent Publication (Kokai) Nos. 63-285140(1988) and 2-163108(1990)]. However, copolymers of this class which have been previously used, exhibit only small improvement in slump loss or caused excessive set retardation to the treated cement composition.

It has now been found that certain copolymer compositions described below having a specified molecular structure have remarkable effectiveness for the prevention of slump loss without causing significant set retardation.

SUMMARY OF THE INVENTION

25 The present invention is directed to a cement admixture composition which requires the use of certain alkenyl ether/polyalkenyl ether/maleic anhydride copolymers.

The specific cement admixture compositions of this invention are alkenyl ether/polyalkenyl ether/maleic anhydride copolymer and mixtures thereof, as fully described below. They have been unexpectedly found to impart a high degree of slump loss over a sustained period of time, dramatically improving workability and applicability while not imparting any significant set retardation to the treated composition.

DETAILED DESCRIPTION

35 The present invention is directed to a cement admixture which has been unexpectedly found to provide a high flowability to cement compositions such as concrete and cement mortar, provide the high flowability over an extended period of time without imparting a significant delay in the curing (set) of the cement composition. This combination of properties has been unexpectedly achieved with the presently described cement admixture compositions.

The admixture composition of this invention is a novel composition for cement which has been unexpectedly found to impart the highly desired property of inhibition of slump-loss. The composition may be composed of one or more copolymer(s) of a combination of an alkenyl ether represented by the general formula (I),



45 wherein, A^1O is one, or a mixture of two or more oxyalkylene group, each having 2 or 3 carbon atoms, said groups, which may be added in block or random fashion;

R^1 is an alkenyl group having 2 to 5 carbons;

R^2 is an alkyl group having 1 to 4 carbons; and

m is an average number of adduct mols of the oxyalkylene groups of from 20 to 150,

50 a polyalkenyl ether represented by the general formula (II),



wherein Z is a residual group of a compound having 2 to 8 hydroxyl groups;

55 A^2O is one, or a mixture of two or more oxyalkylene groups, each having 2 or 3 carbon atoms, said groups may be added in block or random fashion;

R^3 is an alkenyl group having 2 to 5 carbons, n is an average number of adduct mols of the oxyalkylene groups having a value of 1 to 1000; and;

a has a value of 2 to 8,

and maleic anhydride, as the anhydride, its hydrolysis products, or salts of the hydrolysis products.

The ratio of equivalency of copolymerizable double bonds of the component represented by the general formula (I) and the component represented by the general formula (II) is 99:1-60:40, the ratio of equivalency of the sum of the component represented by the general formula (I) and the component represented by the general formula (II) to maleic anhydride is 30:70-70:30. The weight average molecular weight of said copolymer(s) is from 2,000 to 1,000,000.

The copolymers of this invention, their hydrolysis products, or the salts of said hydrolysis products, unlike conventional dispersants for cement, do not show decrease of flowability with respect to time. In many instances, treated cement compositions increase in flowability. Therefore, it can allow production of concrete having excellent property in inhibition of slump-loss when used alone. The present admixture can be also used in combination with existing cement dispersants.

In addition, the admixtures of the present invention do not retard setting nor cause a decrease in the strength after curing of cement compositions which have been so treated.

In the above-described general formula (I) and the above-described general formula (II), the alkenyl groups having 2-5 carbons represented by R^1 and R^3 , respectively, include, for example, vinyl, allyl, methallyl 1,1-dimethyl-2-propenyl, and 3-methyl-3-butenyl groups and the like. The allyl group is most preferred.

In above-described general formula (I) and above-described general formula (II), the oxyalkylene group having 2-3 carbons represented by A^1O and A^2O , respectively, include, for example, oxyethylene and oxypropylene groups with oxyethylene group being most preferred.

In above-described general formula (I), the alkyl group having 1-4 carbons represented by R^2 may be selected for example, from methyl, ethyl, propyl, isopropyl, butyl, isobutyl, and tertiary butyl groups and the like. When the alkyl group has more than four carbon atoms, the amount of air entrainment in the treated mortar or concrete composition is increased. Therefore, it is desirable to select an alkyl group having 1 to 4 carbons if low air entrainment is desired.

The average number of adduct mols (m) of oxyalkylene group with respect to the above-described general formula (I), can be chosen from 20-150. Generally, as the value for m increases, one obtains a lower delay of setting and a higher effect in increasing the slump with time. It is preferred to select the m value from 30 - 120.

Examples of compounds providing the residual group (Z) containing 2-8 hydroxyl groups with respect to the above-described general formula (II) are polyvalent phenols, such as catechol, resorcinol, hydroquinone, phloroglucin and the like; polyvalent alcohols, such as ethyleneglycol, propyleneglycol, butyleneglycol, dodecyleneglycol, octadecyleneglycol, neopentylglycol, styreneglycol, glycerin, diglycerin, polyglycerin, trimethylolethane, trimethylolpropane, 1,3,5-pentanetriol, erythritol, pentaerythritol, dipentaerythritol, sorbitol, sorbitan, solbide, sorbitol/glycerin condensation products, adonitol, arabitol, xylitol, mannitol and the like; sugars such as xylose, arabinose, ribose, rhamnose, glucose, fructose, galactose, mannose, sorbose, cellobiose, maltose, isomaltose, trehalose, raffinose, sucrose, gentianose, melecitose, and the like; and esterified or partially esterified products thereof.

The average number of adduct mols (n) of the oxyalkylene group added as shown in the above-described general formula (II) can be selected from 1 to 1,000. Generally, copolymers having components with higher n values tend to increase the viscosity of the copolymer during its production while providing only minor slump-improving property with respect to increase in the value of n. Therefore, it is preferred to choose copolymers with n of from 1 - 200.

Ratio of equivalency of the copolymerizable double bonds of the compound represented by the general formula (I) and the compound represented by the general formula (II) may be selected from 99:1-60:40. To obtain a copolymer that has excellent slump-sustainability and slump-improving properties, it is important to control the average number of mols (m) of the oxyalkylene group in the general formula (I) and also the ratio of equivalency of the copolymerizable double bonds in the compound represented by the general formula (I) and the compound represented by the general formula (II). Generally, it is preferred that the larger the value of m in the general formula (I), the lower the amount of component represented by the general formula (I) in the resultant copolymer. On the other hand, when the value of m is small, it is preferred to utilize copolymers having higher amounts of component represented by the general formula (I).

Although excellent slump-sustaining properties can be achieved with the copolymer with sufficiently large m value in the general formula (I) and obtained without using a large amount of component of the general formula (II), production of such co-polymerization cannot be carried out easily.

In contrast, copolymers containing component of the general formula (I) and component of the general formula (II) which can achieve a high level of slump sustainability are readily produced and, therefore, the desired property can be readily obtained by the present invention.

The copolymer is characterized by having the capability of improving initial slump of the cement composition and also increasing the slump with time. The particular mode of application of the copolymer is not critical and can be decided by those skilled in the art depending on the types of cement or aggregates being used, whether applied by itself, or by combining it with other cement admixtures.

Cement admixtures that can be used in combination with the subject copolymer include conventional cement dis-

persants, such as naphthalene sulfonic acid/formaldehyde condensates, sulfonated melamine resins, lignin sulfonic acid, aminosulfonic acid, hydroxycarboxylic acid, ethylenically unsaturated dicarboxylic anhydrides, copolymers of linear or cyclic olefins having 4-6 carbon atoms, polycarboxylic acid, and the like; and one, or a mixture of two or more copolymers of maleic anhydride and the component represented by the general formula (I), such as disclosed in Japanese Kokai Patent SHO 63-285140 (1988) or Japanese Kokai Patent HEI 2-163108 (1990), its hydrolysis products, or the salts of its hydrolysis products, and the like.

However, desired properties achievable by the present copolymer may not be highly exhibited when combined with certain conventional dispersants, especially when such dispersants are used in large amounts. If these aspects are taken into consideration, it is most desirable to combine the present copolymer used with the polycarboxylic acid cement dispersants, or with copolymers of maleic anhydride and the component represented by the general formula (I), as disclosed in Japanese Kokai Patent SHO 63-285140 (1988) and Japanese Kokai Patent HEI 2-163108 (1990), its hydrolysis products or the salts of its hydrolysis products. Such conventional dispersant combinations exhibit no or minor adverse effect on the presently achieved properties.

The cement admixture composition disclosed herein can be used together with other known cement additives, such as air entrainers, waterproofing agent, strength enhancers, curing accelerators, antifoam agents and the like may be added and used.

The copolymer of maleic anhydride and the component represented by the general formula (I) and the component represented by the general formula (II) can be formed easily by copolymerization using a peroxide catalyst. The ratio of the equivalency of the sum of copolymerisable double bonds of the component represented by the general formula (I) and the component represented by the general formula (II), to maleic anhydride is selected from 30:70-70:30, preferably 50:50. In certain cases, other copolymerisable components, such as styrene, α -olefin, or vinyl acetate and the like can be used to provide the total combined amount of such monomers is no more than 30 weight percent during preparation of the copolymer. Hydrolysis and partial hydrolysis products of the present copolymer are products which contain at least some maleic acid units which resulted from hydrolysis of the copolymerised maleic anhydride units.

Salts of the hydrolysis products of the copolymer are those formed from the salts of the maleic acid units, and alkali metal salts, such as lithium salts, sodium salts, potassium salts, alkaline earth metal salts, such as magnesium salts and calcium salts, as well as ammonium salts and organic amine salts.

Weight average molecular weight of the copolymer is selected from 2,000-1,000,000, and preferably from 10,000-100,000.

The cement admixture composition of this invention can be used in various types of cements such as ordinary Portland cement, high early strength cement, ultra high early strength cement, blast-furnace slag cement, moderate heat cement, fly ash cement, and sulfate-resisting cement and the like; as well as other water-curable materials, such as gypsum and the like.

The presently described co-polymer admixture can be added to the cement composition through various means. For example, the subject copolymer can be added directly to the hydraulic cement as part of the water forming the initial cement composition or to the final composition, just prior to use. The exact mode of application will be determined by the particular application.

The cement admixture composition of this invention shows a high flowability without causing any significant retardation to the set time of cement composition such as mortar or concrete. In addition, the present admixture composition provides excellent inhibition of slump-loss and, thereby, significantly improves workability of cement compositions used in construction or building-related works.

The cement admixture composition of the present invention can be used for a variety of applications such as, for example, a fluidizing agent for ready-mixed concrete, a high-range AE water-reducing agent, or a high-range water-reducing agent for production of secondary concrete products.

The following examples are given for illustrative purposes only and are not meant to be a limitation on the invention, as defined by the appended claims. All parts and percentages are by weight unless otherwise indicated.

Copolymers of maleic anhydride, component of the general formula (I), and component of the general formula (II) were prepared using the procedure disclosed in Japanese Kokai Patent HEI 2-297411 (1989), as shown by the following examples:

EXAMPLE I

The following ingredients were placed in a four-necked flask equipped with a condenser, a N_2 gas inflow tube, a thermometer and an agitating device. Copolymerization reaction was carried out by raising the temperature of the flask to 80-90°C while continuously agitating for 7 hours under a N_2 gas atmosphere.

Alkenyl ether (polyoxyethylene monoallyl monomethyl ether; number of mols of ethylene oxide added = 33 mols)	573.0g
Dialkenyl ether (polyoxyethylene diallyl ether; number of mols of ethylene oxide added = 33 mols)	55.5 g
Maleic anhydride	43.9 g
Benzoyl peroxide	4.5 g
Toluene	104.8 g

At the completion of the reaction, toluene was removed by distillation at 110°C under a reduced pressure of about 10 mm Hg, to obtain a brown-colored copolymer which was a solid at room temperature [labelled Copolymer (a)].

EXAMPLE 2

The following ingredients were placed in a four-necked flask equipped with a condenser, a N₂ gas inflow tube, a thermometer and an agitating device. Copolymerization reaction was carried out by raising the temperature of the flask to 80-90°C while continuously agitating for 7 hours under a N₂ gas atmosphere.

Alkenyl ether (polyoxyethylene monoallyl monomethyl ether; number of mols of ethylene oxide added = 33 mols)	573.0 g
Dialkenyl ether (polyoxyethylene diallyl ether; number of mols of ethylene oxide added = 33 mols)	102.4 g
Maleic anhydride	49.8 g
Benzoyl peroxide	5.2 g
Toluene	112.6 g

After the reaction, toluene was removed by distillation at 110°C under a reduced pressure of about 10 mm Hg, to obtain a brown-colored copolymer which was a solid at room temperature [labelled Copolymer (b)].

EXAMPLE 3

The following ingredients were placed in a four-necked flask equipped with a condensor, a N₂ gas inflow tube, a thermometer and an agitating device, and polymerization reaction was carried out by raising the temperature of the flask to 90-100°C while continuously agitating for 3 hours under a N₂ gas atmosphere.

Alkenyl ether (polyoxyethylene monoallyl monomethyl ether; number of mols of ethylene oxide added = 91 mols)	800.0 g
Dialkenyl ether (polyoxyethylene diallyl ether; number of mols of ethylene oxide added = 33 mols)	20.7 g
Maleic anhydride	21.9 g
Tertiary Butyl peroxide-2-ethyl hexanoate	4.8 g
Toluene	136.8 g

EP 0 619 277 B1

After the reaction, toluene was removed by distillation at 110°C under a reduced pressure of about 10 mm Hg, to obtain a brown-colored copolymer which was a solid at room temperature [labelled Copolymer (c)].

EXAMPLE 4

The following ingredients were placed in a four-necked flask equipped with a condenser, a N₂ gas inflow tube, a thermometer and an agitating device, and copolymerization reaction was carried out by raising the temperature of the flask to 90-100°C while continuously agitating for 3 hours under a N₂ gas atmosphere.

Alkenyl ether (polyoxyethylene monoallyl monomethyl ether; number of mols of ethylene oxide added = 115 mols)	2500 g
Dialkenyl ether (polyoxyethylene diallyl ether; number of mols of ethylene oxide added = 33 mols)	24.1 g
Maleic anhydride	50.8 g
Benzoyl peroxide	15.0 g
Toluene	420.7 g

After the reaction, toluene was removed by distillation at 110°C under a reduced pressure of about 10 mm Hg, to obtain a brown-colored copolymer which was a solid at room temperature [labelled Copolymer (d)].

EXAMPLE 5

The following ingredients were placed in a four-necked flask equipped with a condenser, a N₂ gas inflow tube, a thermometer and an agitating device, and copolymerization reaction was carried out by raising the temperature of the flask to 90-100°C and continuously agitating for 3 hours under a N₂ gas atmosphere.

Alkenyl ether (polyoxyethylene monoallyl monomethyl ether; number of mols of ethylene oxide added = 115 mols)	2500 g
Dialkenyl ether (polyoxyethylene diallyl ether; number of mols of ethylene oxide added = 200 mols)	138.3 g
Maleic anhydride	50.8 g
Benzoyl peroxide	15.0 g
Toluene	439.7 g

After the reaction, toluene was removed by distillation at 110°C under a reduced pressure of about 10 mm Hg, to obtain a brown-colored copolymer which was a solid at room temperature [labelled Copolymer (e)].

EXAMPLE 6

The following ingredients were placed in a four-necked flask equipped with a condenser, a N₂ gas inflow tube, a thermometer and an agitating device, and copolymerization reaction was carried out by raising the temperature of the flask to 85-90°C and continuously agitating for 3 hours under a N₂ gas atmosphere.

Alkenyl ether (polyoxyethylene polyoxypropylene monoallyl monobutyl ether; number of mols of ethylene oxide added = 57 mols; number of mols of propylene oxide added = 57 mols; by random addition)	3400 g
Dialkenyl ether (polyoxyethylene diallyl ether; number of mols of ethylene oxide added = 33 mols)	49.4 g
Maleic anhydride	62.5 g
Azobisisobutyronitrile	12.5 g
Toluene	574.9 g

After the reaction, toluene was removed by distillation at 110°C under a reduced pressure of about 10 mm Hg, to obtain a brown-colored copolymer which was a solid at room temperature [labelled Copolymer (f)].

EXAMPLE 7

The following ingredients were placed in a four-necked flask equipped with a condenser, a N₂ gas inflow tube, a thermometer and an agitating device, and copolymerization reaction was carried out by raising the temperature of the flask to 75-85°C and continuously agitating for 3 hours under a N₂ gas atmosphere.

Alkenyl ether (polyoxyethylene monomethallyl monomethyl ether; number of mols of ethylene oxide added = 33 mols)	3076 g
Trialkenyl ether (trimethallyl ether of glycerin/ethylenoxide addition product; number of mols of ethylenoxide added = 33 mols)	72.6 g
Maleic anhydride	208.5 g
Azobisisobutyronitrile	14.7 g
Toluene	524.8 g

After the reaction, toluene was removed by distillation at 110°C under a reduced pressure of about 10 mm Hg, to obtain a brown-colored copolymer which was a solid at room temperature (labelled Copolymer (g)).

Each of the copolymers were analyzed and the determined description of each copolymer is given in Table 1 below.

Table 1

Co-polymer	Compound of the general formula (I)	Compound of the general formula (II)	Weight average molecular weight	Equivalent ratio of copolymerizable double bonds in compound (I) and compound (II)
(a)	$\text{CH}_2=\text{CHCH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_{33}\text{CH}_3$	$\text{CH}_2=\text{CHCH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_{33}\text{CH}_2\text{CH}=\text{CH}_2$	43,000	84/16
(b)	$\text{CH}_2=\text{CHCH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_{33}\text{CH}_3$	$\text{CH}_2=\text{CHCH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_{33}\text{CH}_2\text{CH}=\text{CH}_2$	78,000	74/26
(c)	$\text{CH}_2=\text{CHCH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_{91}\text{CH}_3$	$\text{CH}_2=\text{CHCH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_{33}\text{CH}_2\text{CH}=\text{CH}_2$	53,000	88/12
(d)	$\text{CH}_2=\text{CHCH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_{115}\text{CH}_3$	$\text{CH}_2=\text{CHCH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_{33}\text{CH}_2\text{CH}=\text{CH}_2$	62,000	94/6
(e)	$\text{CH}_2=\text{CHCH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_{115}\text{CH}_3$	$\text{CH}_2=\text{CHCH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_{200}\text{CH}_2\text{CH}=\text{CH}_2$	68,000	94/6
(f)	$\text{CH}_2=\text{CHCH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_{57}(\text{CH}_2\text{CHO})_{57}\text{C}_4\text{H}_9$	$\text{CH}_2=\text{CHCH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_{33}\text{CH}_2\text{CH}=\text{CH}_2$	82,000	90/10
(g)	$\text{CH}_2=\text{CHCH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_{33}\text{CH}_3$	$\text{CH}_2=\text{CHCH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_{33}\text{CH}_2\text{CH}=\text{CH}_2$	97,000	94/6

EXAMPLES 8 - 17**PREPARATION OF CONCRETE COMPOSITION**

Based on the formula illustrated in Table 2 below, 40 litres of concrete compositions and cement admixture agent, as shown in Table 3 below were added in a 50 litre capacity forced blending mixer, and they were blended for 90 seconds to prepare a fluidized concrete that had slump of 18 cm and air content of 4-5% (an air entrainer agent AEA available from Denka-Grace K.K. was used to bring the air content to the target level).

After blending was completed, the blend was discharged into a blending boat and it was worked over several times. Change of slump and air content with time was determined immediately after blending, 30 minutes later and 60 minutes later. Method for testing slump, air content, setting time, and compression strength, and method of preparation of test sample for testing the compression strength were based on JIS A6204. Results of the testing are presented in Table 4.

Comparative Examples 1-5

Following the procedure of Examples 8 - 17 described above, fluidized concretes were prepared for comparison. The composition of each Comparative Example are given in Table 3 below and the results of Testing are presented in Table 4.

Table 2

Formula						
Type of concrete	W/C [%]	S/S+G [%]	Unit Amount [kg/m ³]			
			C	W	S	G
Plain	0.64	0.50	320	205	850	876
Evaluation	0.54	0.48	320	166	866	965
Materials Used Cement (C): Ordinary Portland cement (an equi-amount mixture of 3 brands; Specific Gravity = 3.16) Water (W): Tap Water Fine aggregate (S): Sand from Ohi River in Japan (Specific Gravity = 2.60; Fineness modulus = 2.76) Coarse aggregate (G): Crushed stone produced at Oume in Tokyo (Specific Gravity = 2.68; Fineness modulus = 6.60)						

Table 3

Group	Type of cement admixture agent	Amount added (wt.%, based on cement)
Example 8	Copolymer (a)	0.42
Example 9	Copolymer (b)/PC(a)	0.30/0.10
Example 10	Copolymer (c)/PC(a)	0.20/0.05
Example 11	Copolymer (c)/PC(b)	0.20/0.07
Example 12	Copolymer (c)/LS	0.20/0.15
Example 13	Copolymer (c)/NSFC	0.20/0.20
Example 14	Copolymer (d)/PC(a)	0.15/0.08
Example 15	Copolymer (e)/PC(a)	0.13/0.09
Example 16	Copolymer (f)/PC(a)	0.15/0.09
Example 17	Copolymer (g)/PC(a)	0.15/0.15

Table 3 (continued)

Group	Type of cement admixture agent	Amount added (wt.%, based on cement)
Comparative Ex. 1	PC(a)	0.19
Comparative Ex. 2	PC(b)	0.23
Comparative Ex. 3	NSFC	0.60
Comparative Ex. 4	LS	0.60
Comparative Ex. 5	Copolymer (c)	0.27

PC(a): Ratio of equivalency of the copolymerizable double bonds of the compound represented by the general formula (I) where R¹ is CH₂=CHCH₂, R² is -CH₃, A¹O is -C₂H₄O-, and m is 33, and maleic anhydride is 1:1, and weight average molecular weight is 20,000. This is the Ca salt of the copolymer having such composition.
 PC(b): Calcium Polycarboxylate cement dispersant (commercial product)
 NSFC: Calcium naphthalene sulfonate cement dispersant (commercial product)
 LS: Calcium lignin sulfonate cement dispersant (commercial product)

Table 4

Group	Immediately after		30 Minutes later		60 Minutes later		Delay of setting (*3) [Minutes]	Compression strength after 28 days [kg/cm ²]
	Slump [cm]	Air [%]	Slump [cm]	Air [%]	Slump [cm]	Air [%]		
Example 8	18.0	4.6	18.0	4.4	17.0	4.2	+85	422
Example 9	18.5	4.3	18.0	4.3	17.5	4.0	+80	425
Example 10	18.0	4.2	19.0	4.2	18.5	4.1	+45	438
Example 11	18.5	4.6	19.0	4.4	18.0	4.2	+55	433
Example 12	18.5	4.2	18.0	4.4	17.0	4.4	+80	415
Example 13	19.0	4.7	18.0	4.3	17.0	4.1	+60	418
Example 14	18.0	4.1	19.0	4.2	18.5	4.3	+45	435
Example 15	17.5	4.3	19.0	4.1	19.0	4.1	+40	440
Example 16	18.0	4.5	18.5	4.4	18.0	4.5	+50	428
Example 17	18.5	4.4	19.0	4.6	18.5	4.3	+65	435
Comparative Ex. 1	18.5	4.3	14.5	4.5	12.0	4.3	+80	422
Comparative Ex. 2	19.0	4.5	16.0	4.5	11.5	4.2	+85	418
Comparative Ex. 3	18.5	4.8	14.5	4.4	8.5	3.9	+30	422
Comparative Ex. 4	18.5	4.3	16.5	4.6	11.0	4.5	+105	408
Comparative Ex. 5	18.0	4.2	>25 ⁽⁴⁾	2.2	23.5	2.8	+40	440

3) Delay time, compared to plain concrete.

4) Segregation has been confirmed

Claims

1. An admixture for a cement composition comprising at least one copolymer composed of a combination of an alkenyl ether represented by the general formula (I)



wherein A^1O is one or a mixture of oxyalkylene groups having 2 to 3 carbons;

R^1 is an alkenyl group having 2 to 5 carbons;

R^2 is an alkyl group having 1 to 4 carbons; and m represents an average number of mols of the oxyalkylene groups and has a numerical value of from 20 to 150,

a polyalkenyl ether represented by the general formula (II),



wherein Z is a residual group of a compound having 2 to 8 hydroxyl groups,

A^2O is one or a mixture of oxyalkylene groups having 2 to 3 carbons;

R^3 is an alkenyl group having 2 to 5 carbons; n represents an average number of mols of the oxyalkylene groups and has a numerical value of from 1 to 1000; and a has a value of 2 to 8,

and maleic anhydride, its hydrolysed product or salts of its hydrolysed products, where the ratio of equivalency of copolymerisable double bonds of the component represented by the general formula (I) and the component represented by the general formula (II) is 99:1-60:40, the ratio of equivalency of the sum of the component represented by the general formula (I) and the component represented by the general formula (II) to maleic anhydride, its hydrolysed product or salts thereof is 30:70-70:30, and the copolymer has a weight average molecular weight of from about 2,000-1,000,000.

2. The admixture according to claim 1 wherein the groups A^1O and A^2O each individually represent a mixture of oxyalkylene groups and are present in block or random configuration.
3. The admixture according to claim 1 or claim 2 wherein one of the groups A^1O and A^2O each independently represents oxyethylene.
4. The admixture according to any preceding claim wherein the symbol m of the Formula I represents 30 to 120; and the symbol n of Formula II represents 1 to 200.
5. The admixture according to any preceding claim wherein the copolymer has a weight average molecular weight of from about 10,000 to 100,000.
6. The admixture according to any preceding claim wherein the admixture comprises a major amount of said copolymer in combination with a minor amount of a cement additive selected from dispersants, air entrainers, air detrainers, waterproofing agents, strength enhancers, curing accelerators and antifoam agents or mixtures thereof.
7. An improved cement composition capable of exhibiting an inhibition to slump loss with respect to time comprising a hydraulic cement, aggregate, water and the admixture according to any preceding claim.
8. The improved cement composition of claim 7 wherein the aggregate is composed of sand and stone to form a concrete.
9. A method for forming a cement composition comprising mixing a hydraulic cement, aggregate, water and an admixture according to any of claims 1 to 6.
10. Use of a copolymer as defined in any of claims 1 to 6 for the manufacture of an admixture for inhibiting slump loss of a cement.

Patentansprüche

1. Zumischung für eine Zementzusammensetzung, die mindestens ein Copolymer umfaßt, das aus einer Kombination aus Alkenylether mit der allgemeinen Formel (I)



in der A^1O eine oder eine Mischung aus Oxyalkylengruppen mit 2 bis 3 Kohlenstoffatomen ist,
 R^1 eine Alkenylgruppe mit 2 bis 5 Kohlenstoffatomen ist,
 R^2 eine Alkylgruppe mit 1 bis 4 Kohlenstoffatomen ist und m eine Durchschnittsanzahl der Mol der Oxyalkylen-
gruppen bedeutet und einen Zahlenwert von 20 bis 150 hat,

Polyalkenylether mit der allgemeinen Formel (II)



wobei Z eine Restgruppe einer Verbindung mit 2 bis 8 Hydroxylgruppen ist,
 A^2O eine oder eine Mischung aus Oxyalkylengruppen mit 2 bis 3 Kohlenstoffatomen ist,
 R^3 eine Alkenylgruppe mit 2 bis 5 Kohlenstoffatomen ist, n eine Durchschnittsanzahl der Mol der Oxyalkylen-
gruppen bedeutet und einen Zahlenwert von 1 bis 1000 hat und a einen Wert von 2 bis 8 hat,

und Maleinsäureanhydrid, dessen hydrolysiertem Produkt oder Salzen seiner hydrolysierten Produkte zusammen-
gesetzt ist, wobei das Äquivalenzverhältnis von copolymerisierbaren Doppelbindungen der durch die allgemeine
Formel (I) wiedergegebenen Komponente und der durch die allgemeine Formel (II) wiedergegebenen Komponente
99:1 bis 60:40 beträgt, das Äquivalenzverhältnis der Summe der durch die Formel (I) wiedergegebenen Kompo-
nente und der durch die Formel (II) wiedergegebenen Komponente zu Maleinsäureanhydrid, dessen hydrolysier-
tem Produkt oder Salzen derselben 30:70 bis 70:30 beträgt, und das Copolymer ein durchschnittliches
Molekulargewicht (Gewichtsmittel) von etwa 2000 bis 1 000 000 hat.

2. Zumischung nach Anspruch 1, bei der die Gruppen A^1O und A^2O jeweils individuell eine Mischung von Oxyalky-
lengruppen bedeuten und in Block- oder statistischer Konfiguration vorliegen.
3. Zumischung nach Anspruch 1 oder Anspruch 2, bei der eine der Gruppen A^1O und A^2O jeweils unabhängig Oxye-
thylen bedeutet.
4. Zumischung nach einem der vorhergehenden Ansprüche, bei der das Symbol m der Formel I 30 bis 120 bedeutet
und das Symbol n der Formel II 1 bis 200 bedeutet.
5. Zumischung nach einem der vorhergehenden Ansprüche, bei der das Copolymer ein durchschnittliches Molekular-
gewicht (Gewichtsmittel) von etwa 10 000 bis 100 000 aufweist.
6. Zumischung nach einem der vorhergehenden Ansprüche, bei der die Zumischung eine größere Menge des Copo-
lymers in Kombination mit einer geringeren Menge eines Zementadditivs ausgewählt aus Dispergiermitteln, Luft-
porenbildnern, Entlüftungsmitteln, wasserfestmachenden Mitteln, Festigkeitserhöhungsmitteln,
Härtungsbeschleunigern und Antischaummitteln oder Mischungen derselben umfaßt.
7. Verbesserte Zementzusammensetzung, die eine Verhinderung des Setzmaßverlustes in Bezug auf die Zeit zeigen
kann und hydraulischen Zement, Zuschlag, Wasser und die Zumischung gemäß einem der vorhergehenden
Ansprüche umfaßt.
8. Verbesserte Zementzusammensetzung nach Anspruch 7, bei der der Zuschlag aus Sand und Stein zusammenge-
setzt ist, um Beton zu bilden.
9. Verfahren zur Bildung einer Zementzusammensetzung, bei dem hydraulischer Zement, Zuschlag, Wasser und eine
Zumischung gemäß einem der Ansprüche 1 bis 6 gemischt werden.
10. Verwendung eines Copolymers gemäß der Definition in einem der Ansprüche 1 bis 6 zur Herstellung einer Zumi-
schung, um den Setzmaßverlust von Zement zu verhindern.

Revendications

1. Mélange pour une composition de ciment comprenant au moins un copolymère composé d'une combinaison d'un alkényl éther représenté par la formule générale (I)



où A¹O est un groupe ou un mélange de groupes oxyalkylène ayant de 2 à 3 carbones;

R¹ est un groupe alkényle ayant 2 à 5 carbone;

R² est un groupe alkyle ayant 1 à 4 carbones; et m représente le nombre moyen de moles des groupes oxyalkylène et a une valeur numérique de 20 à 150,

un polyalkényl éther représenté par la formule générale (II),



où Z est un groupe résiduel d'un composé ayant 2 à 8 groupes hydroxyle,

A²O est un groupe ou un mélange de groupes oxyalkylène ayant 2 à 3 carbones;

R³ est un groupe alkényle ayant 2 à 5 carbones; n représente le nombre moyen de moles des groupes oxyalkylène et a une valeur numérique de 1 à 1000; et a a une valeur de 2 à 8,

et de l'anhydride maléique, son produit hydrolysé ou les sels de ces produits hydrolysés, où le rapport d'équivalence des doubles liaisons copolymérisables du composant représenté par la formule générale (I) et du composant représenté par la formule générale (II) est de 99:1 à 60:40, le rapport d'équivalence de la somme du composant représenté par la formule générale (I) et du composé représenté par la formule générale (II) à l'anhydride maléique, son produit hydrolysé ou ses sels est de 30:70 à 70:30, et le copolymère a un poids moléculaire moyen en poids d'environ 2 000 à 1 000 000.

2. Mélange selon la revendication 1 dans lequel les groupes A¹O et A²O représentent chacun individuellement un mélange de groupes oxyalkylène et sont présents en une configuration bloc ou aléatoire.

3. Mélange selon la revendication 1 ou la revendication 2 dans lequel un des groupes A¹O et A²O représente chacun indépendamment un oxyéthylène.

4. Mélange selon l'une quelconque des revendications précédentes dans lequel le symbole m de la Formule I représente 30 à 120; et le symbole n de la Formule II représente 1 à 200.

5. Mélange selon l'une quelconque des revendications précédentes dans lequel le copolymère a un poids moléculaire moyen en poids d'environ 10 000 à 100 000.

6. Mélange selon l'une quelconque des revendications précédentes dans lequel le mélange comprend une quantité majoritaire dudit copolymère en combinaison avec une quantité minoritaire d'un additif de ciment sélectionné parmi des dispersants, des entraîneurs d'air, des agents enlevant l'air, des agents d'imperméabilité, des exhausteurs de résistance, des accélérateurs de durcissement et des agents anti-mousse ou des mélanges de ceux-ci.

7. Composition de ciment améliorée capable de présenter une inhibition de la perte de hauteur d'affaissement par rapport au temps comprenant un ciment hydraulique, un agrégat, de l'eau et le mélange selon l'une quelconque des revendications précédentes.

8. Composition de ciment améliorée selon la revendication 7 dans laquelle l'agrégat est composé de sable et de pierre pour former un béton.

9. Méthode pour former une composition de ciment comprenant le mélange d'un ciment hydraulique, d'un agrégat, d'eau et d'un mélange selon l'une quelconque des revendications 1 à 6.

10. Utilisation d'un copolymère tel que défini dans l'une quelconque des revendications 1 à 6 pour la fabrication d'un mélange pour inhiber la perte de hauteur d'affaissement d'un ciment.